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FREE-RADICAL REACTIONS OF 2-ETHOXY-1,3-OXATHIOLANE

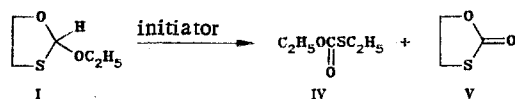
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Homolytic reactions of 2-ethoxy-1,3-oxathiolane in the presence of benzoyl peroxide and tert-butyl peroxide in chlorobenzene have been studied. The principal reaction products are diethyl monothiocarbonate and 1,3-oxathiolane-2-one. The yields and ratios of the products are temperature-dependent.

It has previously been shown that straight-chain and cyclic orthoesters and their nitrogen analogs are converted in the presence of radical initiators into straight-chain and cyclic carbonates and dialkylcarbamate esters, respectively [1, 2].

We have examined for the first time the liquid-phase homolytic reactions of the analogous 2-ethoxy-1,3-oxathiolane (I) on treatment with benzoyl peroxide (II) and tert-butyl peroxide (III) in chlorobenzene. Under these conditions, (I) affords in parallel diethyl monothiocarbonate (IV) and 1,3-oxathiolan-2-one (V).



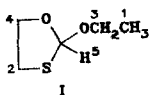
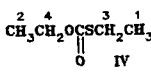

In the absence of an initiator, (IV) and (V) were not formed.

The experimental results on the conversion and yields of the products of the free-radical reactions of 2-ethoxy-1,3-oxathiolane are given in Table 1.

TABLE 1. Yields of Products of Free-Radical Reactions of (I) [concentration of (I) 4.0, (II) 0.1, and (III) 0.3 mole/liter; solvent chlorobenzene]

Reaction conditions			Concentration, mole/liter			Conversion of (I), %	Yield on (I) reacted, %	
temperature, °C	initiator	time, h	I	IV	V		IV	V
80	II	5	3,2	0,45	0,15	20	56	20
100	II	4	2,0	1,30	0,4	50	65	20
120	III	2	2,4	1,05	0,20	40	60	12

TABLE 2. ^1H NMR Spectra and Physicochemical Constants of 2-Ethoxy-1,3-oxathiolane (I), Diethyl Monothiocarbonate (IV), and 1,3-Oxathiolan-2-one (V)

Compound	Bp, °C (mm Hg)	n_D^{20}	d_4^{20}	δ , ppm from HMDS					Coupling const., Hz
				1	2	3	4	5	
 I	70 (10)	1,4660	1,1103	1,12 t	2,80— 3,10 m	3,48 q	3,90— 4,20 m	6,16 s	7,0
 IV	157	1,4478	1,0125	1,25 t	1,26 t	2,78 q	4,17 q		7,3
 V	110 (9)	1,5126	1,3472	2,75— 3,15 m	3,92— 4,24 m				

EXPERIMENTAL

2-Ethoxy-1,3-oxathiolane (I) was obtained as described in [3]. The purity of the thiolane (I) was checked by IR spectroscopy, and was not less than 98%. Products (IV) and (V) were isolated on a PAKhC-08 preparative chromatograph with a thermal conductivity detector, column 300×0.3 cm, carrier gas helium, flow rate 10 liters/h, column temperature 170°C , evaporator temperature 300°C . Chromatographic phase, 25% Apiezon-L on Chromatone NAW. The structures of the reaction products were established by their PMR spectra (Table 2). The spectral measurements were made on a Tesla BS-497 (100 MHz).

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